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Review

Biochar stability assessment by incubation and modelling: Methods, drawbacks and recommendations

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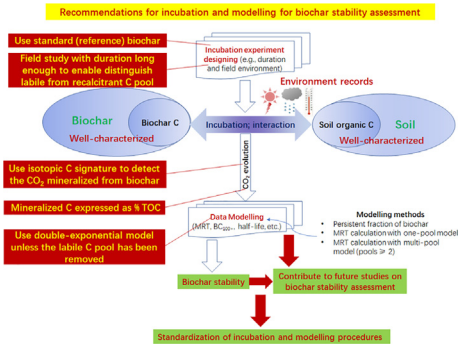
HIGHLIGHTS

- The incubation method has many drawbacks and is slow.
- C isotope is preferable to quantitate the biochar C mineralization.
- Two-pool model with data expressed as % TOC mineralized is preferable.
- Reference standard biochar can facilitate comparison between studies.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochar produced from pyrolysis of biomass is a candidate with great potential for climate change mitigation by carbon sequestration and reduction of greenhouse gases (GHG) emission in soil. Its potential depends considerably on biochar properties. Biochar stability or biochar C recalcitrance is decisive to its carbon storage/sequestration potential in soil. Three groups of methods including: I) biochar C structure or composition analyses, II) biochar oxidation resistance determination, and III) biochar persistence assessment by incubation & modelling, have been developed for evaluation of biochar stability. Amongst, incubation & modelling is the most commonly used one and is the basis of the other two assessment methods. However, the strategies for incubation experiment designing and data modelling significantly influence the biochar stability results. Drastic differences were observed for stability results obtained from different studies partly because of the large flexibility of the incubation & modelling method. Biased biochar stability would be obtained if the method was used improperly. The present review aims to provide comprehensive information on method strategies used for incubation and modelling, followed by discussions on the key issues such as what kind of biochar to use, how the experiment should be designed, how to determine biochar C mineralization, how the mineralization data should be expressed, and what model should be used, for an accurate biochar stability evaluation. In general, incubating biochar at long-term duration, modelling incubation data with double-exponential model, using C isotopic technology for CO_2

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evolution determination with C mineralization data express as percentage of total organic carbon mineralized, applying biochar in the field are favorable to biochar stability assessment. Other strategies such as the use of standard (reference) biochar materials may be effective to improve the assessment.

Contents

1. Introduction

Biochar is a pyrogenic organic carbon material produced from pyrolysis of biomass and it can be used in areas such as agriculture, environment, and energy (Leng et al., 2015; Tan et al., 2017; Wang et al., 2018; Zeng et al., 2018; Zhou et al., 2017). Biochar is being developed as a promising strategy for the mitigation of climate change by carbon sequestration and reduction of greenhouse gases (GHG) emissions in soil (Lehmann, 2007a, 2007b; Lehmann et al., 2006). It has recently been included for the first time as a promising negative emission technology by Intergovernmental Panel on Climate Change (IPCC) in a special report (October 2018). This marks a milestone for biochar as a climate change mitigator. Biochar C sequestration in soil contributes greatly to climate change mitigation as it assumes that biochar C persists on a centennial to millennial time scale. Therefore, biochar stability in soil is a fundamental aspect of this area and many studies have been carried out on this topic.

There are two groups of factors determining the stability of biochar applied in soil: one is the biochar properties, and the other is the soil environment (Leng and Huang, 2018). Biochar stability can be estimated by three methods: I) biochar C structure or composition analyses, II) biochar oxidation resistance determination, and III) biochar persistence evaluation by incubation & modelling. Only method III) gives actual duration of the biochar C in soil. It is the core of biochar stability assessment methods and is the basis of the other two methods (Leng et al., 2019). Whereas, methods I) and II) can only give relative stability rather than actual persistence unless these methods are correlated with method III). Results from methods I) and II), such as ratio of H/C_{org} (ratio of hydrogen and organic C content) (Budai et al., 2013), H_2O_2- and heat-assisted oxidizability (Cross and Sohi, 2013), thermal stability (R_{50}) (Harvey et al., 2012), and proportion of nonaromatic C or degree of aromatic condensation ($-\Delta\delta$) (Singh et al., 2012a), have been correlated with the actual biochar C duration (e.g., mean residence time, MRT) obtained from incubation & modelling (Fig. 1). However, the reliability of these relationships depends directly on the accuracy of the incubation & modelling method. Therefore, the optimization of the method III) is a priority research frontier.

During incubation, the assays of CO_2 evolved from biochar applied in soil or the changes of biochar C amount remained in soil over time can be used to indicate the stability/persistence or mineralization potential of biochar C in soil (Kuzyakov et al., 2014; Weng et al., 2017; Zimmerman, 2010). Accurate assessments to obtain real biochar stability extending the incubation to hundreds of years or even longer are difficult and unfeasible. In order to facilitate the assessment, biochar C mineralization can be modelled by assuming an exponential decay of biochar in soil based on biochar mineralization data during incubation experiment (Kuzyakov et al., 2014; Weng et al., 2017; Zimmerman, 2010). However, due to the flexible incubation experiment designing and data modelling methods, the modelled biochar stability can deviate dramatically from the real one and vary largely between different studies or even within an individual study. Because of the lack of standard incubation & modelling method procedures, justification of a convincible biochar stability is very difficult, particularly for non-specialists.

The objectives of this study are to 1) review the method details of biochar stability assessment by incubation & modelling; 2) identify the drawbacks of this assessment method; 3) recommend

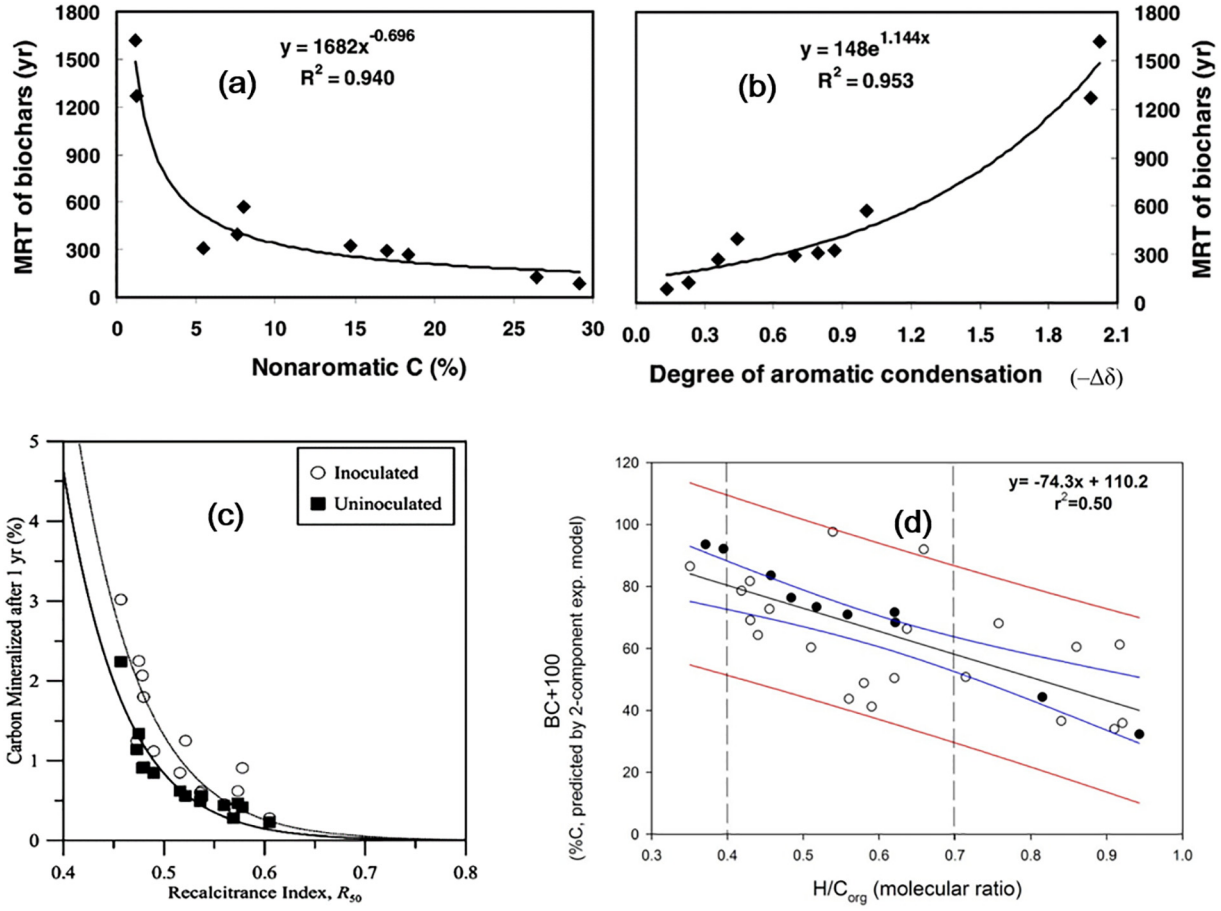

Fig. 1. Relationships between mean residence time (MRT) of biochar C and nonaromatic C proportion (a)/degree of aromatic condensation (b) determined by ^{13}C CP NMR (Singh et al., 2012a), relationship between biochar degradability and thermal recalcitrance R_{50} (c) (Harvey et al., 2012), and relationship between BC_{+100} and H/C_{org} (d) (Budai et al., 2013).

strategies to overcome the drawbacks of the method for more accurate estimation.

2. Biochar stability assessment methods

2.1. Relative persistence of biochar

When biochar is applied in soil, the mass of biochar C in soil will change over time as the incubation (mineralization) proceeds. Therefore, the relative persistence of residual biochar C in soil is a dynamic one. The cumulative loss of biochar C can be obtained by directly analyzing the biochar C mass assuming that all lost C is mineralized, or by calculating from the biochar derived CO_2 evolution.

Because the longest biochar incubation experiments reported were carried out within a decade (Kuzyakov et al., 2014; Weng et al., 2017), which is much shorter than the estimated centennially to millennially half-life of biochar C, the long-term persistent longevity of biochar can only be estimated from modelling. This is a significant constraint that limits the use of the method, and extrapolation is needed. The variation of residual fraction or mineralized fraction of biochar vs. incubation time

Table 1
Different biochar stability proxies obtained from incubation and modelling.

Proxies	Advantages	Disadvantages	Comments
Relative persistent fraction of biochar after incubation	■ Very accurate (real value).	■ Barely applicable because data of several decades even hundreds of years need to be collected.	■ Can be used as control.
Mean residence time (MRT) calculation with one-pool model	■ Easy; ■ Low requirement for data availability (minimum data point: 2).	■ Low accuracy because it uses an average degradation rate for all biochar fractions.	■ MRT is the basis of other methods; ■ Incubation duration, modelling and calculation methods, the application environment (laboratory incubation or field), and biochar C mineralization rate analysis methods (biochar mass loss or CO_2 evolution) can significantly influence the value of MRT.
MRT calculation with multi-pool model	■ Relatively high accuracy compared to MRT determined by one-pool model.	■ High requirement for data availability; the incubation experiment needs to be long enough to distinguish the carbon pools used for modelling	
BC_{+100} (the percentage of organic C in biochar that remains stable in soil for >100 years)	■ A summarized index useful to determine the permanence (100 years) of biochar.	■ Qualitative; ■ It is calibrated by MRT collected from only several studies, and it can be further optimized.	■ It is the basis for using ultimate analysis method (H/C_{org} and/or O/C_{org}) as biochar stability proxies; ■ Stock BC_{+100} has been used to set up carbon sequestration potentials of biochar.
Half-life time (the time that elapses before half of the biochar mineralizes)	■ Relatively high accuracy compared to MRT determined by one-pool model.	■ High requirement for data availability; the incubation experiment needs to be long enough to distinguish carbon pools used for modelling	■ Determined by MRT value (it can be obtained by multiplying the MRT by the natural logarithm of 2 ($t_{1/2}$ = MRT * ln2 or $t_{1/2}$ = ln2 / 02k)).

can be further used for MRT calculation by fitting the data with models. The advantages and disadvantages of methods used for obtaining persistence of biochar in soil by different modelling methods can be seen in Table 1.

2.2. MRT calculation with one-pool model (one-exponential model)

The one-pool model calculation assumes that all C in biochar decays at an average decay rate irrespective of the chemistry of different C fractions. This model is simple and has been widely used by many researchers (Bai et al., 2013; Bruun et al., 2012; Cross and Sohi, 2011; Luo et al., 2011; Zimmerman et al., 2011). The decay rate is the exponent (k, as a function of environmental conditions) in the exponential decay function and has a unit of 1/time, and the biochar remained or mineralized at time t can be expressed as (Lehmann and Joseph, 2015):

$$C_r = C_0 * \exp(-k * t) \quad (1)$$

$$C_m = C_0 * [1 - \exp(-k * t)] \quad (2)$$

where C_r, C_m and C_0 represent biochar C remained and mineralized at time t and the initial amount in the soil, respectively.

$$\mathrm{MRT} = 1/k \quad (3)$$

where k is the decay rate.

MRT is expressed as the inverse of decay rate and it means the average time that biochar can persist from decaying. The decay rate (k) can be obtained from fitting the data to Eq. 1. The instant biochar C decay rate decreases with time because the easily degradable C fraction is mineralized first and then follows the less degradable ones. Therefore, the duration of incubation is pivotal to the MRT calculation. Shorter duration can lead to higher estimated mineralization rate and thus smaller MRT. For example, Gronwald et al. (2016) estimated the mass percentage of biochar C remained in soil by one-exponential model after incubation of 1.2 years, and obtained MRT only about 60 years and 4 years for biochar and hydrochar from pyrolysis and hydrothermal carbonization of *Miscanthus*, respectively. The meta-analysis data of biochar mineralization from 16 studies using one-exponential model resulted in a MRT ranging from <1 year to >750 years, and short-term studies tend to have shorter MRTs (Singh et al., 2012b). The short-term studies mainly capture the fast-mineralizing labile biochar C fraction, resulting in underestimation of biochar stability.

2.3. MRT calculation with multi-pool model (C pools ≥2)

2.3.1. Two-pool model (double-exponential model)

In fact, biochar is composed of a spectrum of chemical structures and arrangements; each with its own degradation rate (Schimmelpfennig and Glaser, 2012; Spokas, 2010). Using a higher number of C pools generally increases the modelling fitness and therefore calculation accuracy. The two-pool model (double-exponential model), which includes a relatively labile and a refractory C pools, is a drastic simplification of the continuum. The two-pool model can be reasonable approximation for data modelling purposes and it is generally more widely used and more accurate for MRT evaluation than the one-exponential model (Bai et al., 2013; Calvelo Pereira et al., 2014; Farrell et al., 2013; Hilscher et al., 2009; Keith et al., 2011; Singh et al., 2012a; Zimmerman, 2010; Zimmerman and Gao, 2013). In the two-pool model, each pool has its mineralization characteristics: labile C pool is generally small and easy to be mineralized while recalcitrant C pool represents the major part of biochar and is resistant to mineralization. The labile C pool generally has an estimated residence time of years to decades, and the recalcitrant C pool generally has an estimated residence time of centuries to millennia. The double-exponential model can be expressed as following (Singh et al., 2012b; Wang et al., 2016; Zimmerman et al., 2011):

$$C_r = C_1 * \exp.(-k_1 * t) + C_2 * \exp(-k_2 * t) \quad (4)$$

$$C_m = C_1 * [1 - \exp(-k_1 * t)] + C_2 * [1 - \exp(-k_2 * t)] \quad (5)$$

$$C_1 + C_2 = C_0 \quad (6)$$

where C_1 and C_2 represent labile and recalcitrant biochar C pool size, respectively. While, k_1 and k_2 represent the mineralization rates of labile and recalcitrant biochar C pool, respectively.

$$\mathrm{MRT\ (labile\ C\ pool)} = 1/k_1 \quad (7)$$

$$\mathrm{MRT\ (recalcitrant\ C\ pool)} = 1/k_2 \quad (8)$$

Zimmerman et al. (2011) found the kinetics of CO_2 efflux from all incubations well-fit to the double-exponential model ($R^2 > 0.97$), and both biochars and soils have much larger size of refractory C pool versus labile C pool. The MRT of refractory C pool can be used as the MRT of the biochar when $C_1 \ll C_2$ and $k_1 \gg k_2$ (Bai et al., 2013). The double-exponential-model estimated MRT of biochar (at 10 °C) using global data set collected in publications consistently exceeds 1000 years for biochars with $H/C_{org} < 0.4$, while MRT > 500 years was found for $0.4 < H/C_{org} < 0.7$ (Lehmann and Joseph, 2015). For the double-exponential model, the duration of experiment is a significant factor to influence the assessment. If the duration is not long enough to distinguish the recalcitrant C pool from the labile one, an underestimation would likely to happen.

2.3.2. Three-pool model

Three-pool model (Eqs. 9–11) has also been used for biochar mineralization modelling and MRT calculation (Herath et al., 2015).

$$C_r = C_1 * \exp(-k_1 * t) + C_2 * \exp(-k_2 * t) + C_3 * \exp(-k_3 * t) \quad (9)$$

$$C_m = C_1 * [1 - \exp(-k_1 * t)] + C_2 * [1 - \exp(-k_2 * t)] + C_3 * [1 - \exp(-k_3 * t)] \quad (10)$$

$$C_1 + C_2 + C_3 = C_0 \quad (11)$$

where C_1, C_2 and C_3 are three different C pool size, and k_1, k_2 and k_3 represent the mineralization rates of the three pools.

$$\mathrm{MRT\ (labile\ C\ pool)} = 1/k_1 \quad (12)$$

$$\mathrm{MRT\ (semi-labile\ C\ pool)} = 1/k_2 \quad (13)$$

$$\mathrm{MRT\ (recalcitrant\ C\ pool)} = 1/k_3 \quad (14)$$

By using three-pool model, MRTs of 244–369 years were obtained for biochars incubated for 510 days (Herath et al., 2015; Lehmann and Joseph, 2015). However, no comparison between the results from three-pool and two-pool/one-pool models was reported.

2.3.3. Power model (logarithmic model)

A logarithmic model proposed by Zimmerman (2010), in which direct correlations were built between the logarithmically transformed experimental degradation rate (k) and incubation time (t) (Eq. 15), is a model trying to work with infinite C pools in biochar. The degradation rate decreases continuously and exponentially as more labile or physically accessible biochar C fraction degrades, leaving behind a progressively more refractory or physically inaccessible residue, and the mineralized biochar at time t can be expressed as Eq. 16 (Zimmerman, 2010).

$$\ln(-k) = m * \ln(t) + b \quad (15)$$

$$C_m = C_0 - C_r = \left(\frac{C_0 e^b}{m+1}\right) * t^{m+1} \ [m > -1] \quad (16)$$

$$C_m = C_0 - C_r = C_0 * e^b * \ \ln(t) \ (m = -1) \quad (17)$$

The results obtained by this method are quite sensitive to small changes in m and b. Therefore, these values are not hard values, but represent realistic biochar decay rates within an order of magnitude (Zimmerman, 2010). The linear regression between logarithmically transformed experimental degradation rate (k) and incubation time (t) is very important to the effectiveness of this method. The half-lives of biochar are in the range of 10^2 and 10^5 years when modelling mineralization data with power model (Fang et al., 2014a; Zimmerman, 2010). Due to the mathematical restrictions and the complexity of this model, it is only scarcely used by investigators for biochar stability assessment.

Considering that biochar C is composed of a continuum of C forms (Schimmelpfennig and Glaser, 2012; Spokas, 2010), rather than a homogeneous material degrading at a constant rate, two-pool model (a recalcitrant C pool and a labile C pool) would be desirable compared with one-pool model. Theoretically, multi-pool (pools > 2) models, particularly the power model with infinite pools, may be more favorable not considering their requirements for longer duration (Herath et al., 2015; Zimmerman and Gao, 2013). However, over-fitting of the multi-pool models is likely to happen when the decomposition rates of different C pools are similar, which should be avoided by using one-pool model (Weihermüller et al., 2018).

2.4. BC_{+100}

Global warming potential of GHG is assessed over a 100-year time horizon and this horizon is commonly used to define permanence in carbon offset markets (IPCC, 2007). The fraction (percentage, %) of C_{org} in biochar which remains stable in soil for >100 years (BC_{+100}) is a rationale proposed by International Biochar Initiative (IBI), a member-based organization led by several outstanding biochar scientists such as Johannes Lehmann, for assessing the C storage value of biochar (Budai et al., 2013). The use of 0.7 as an upper H/C_{org} limit by IBI (IBI, 2015) to differentiate biochar that can be used for carbon sequestration from biomass is based on the relationship between BC_{+100} and H/C_{org} (Singh et al., 2012a; Zimmerman, 2010; Zimmerman and Gao, 2013). By grouping the predicted BC_{+100} values against the corresponding H/C_{org} values, a correlation can be obtained between these two indicators: $BC_{+100} = -74.3 * (H/C_{org}) + 110.3$, $n = 31$, $R^2 = 0.50$. A BC_{+100} value of 50% (meaning 50% of the biochar can be preserved after 100 years) can be conservatively expected from a biochar with H/C_{org} value of <0.7 (95% confidence); a BC_{+100} value of 70% (meaning 70% of the biochar can be preserved after 100 years) can be expected from a biochar with H/C_{org} value of 0.4 (95% confidence) (Budai et al., 2013). The most updated correlation can be expressed as: $BC_{+100} = -42.4 * (H/C_{org}) + 106$ (10 °C) and $BC_{+100} = -61.6 * (H/C_{org}) + 105$ (20 °C) ($R^2 = 0.45$, $n = 43$, $p < 0\ 01$) (Lehmann and Joseph, 2015). However, the relationship between BC_{+100} and H/C_{org} is not such robust to predict the exact biochar stability. On the other hand, it is a conservative indicator to ensure that 50% (biochar with $0.4 < H/C_{org} < 0.7$) or 70% (biochar with $H/C_{org} < 0.4$) of biochar C would be stable in soil within 100 years.

It is worth mentioning that in addition to H/C_{org}, the O/C_{org} ratio is also relevant to biochar stability, and European Biochar Certificate (EBC), a voluntary European industrial standard, made requirements on both H/C_{org} and O/C_{org} (EBC, 2012). The upper O/C_{org} limit of 0.4 is required by EBC for a standard-compliant biochar in addition to the H/C_{org} ratio of <0.7 (EBC, 2012). On the other hand, Schimmelpfennig and Glaser (2012) proposed an upper O/C_{org} limit of 0.4 and H/C_{org} of 0.6, with black carbon >15% C, polyaromatic hydrocarbons lower than soil background values, and surface area > 100 m^2/g for a suitable biochar that can be used for soil amendment and carbon sequestration. Because of the simplicity and easy availability, H/C_{org} and/or O/C_{org} have been widely accepted as effective proxies to biochar stability (EBC, 2012; IBI, 2015).

Stock BC_{+100} (sBC_{+100}, g kg^{-1}) is a C storage value (carbon sequestration potential) that can be obtained by multiplying BC_{+100} with the total C_{org} (Budai et al., 2013). Based on the sBC_{+100} value of biochar, Lehmann and Joseph (2015) proposed a five-class classification to assess the carbon sequestration potential of biochar. The classification of biochar can be made according to the tools posted on website of IBI by inputting the data set of biochar. The Pacific Northwest (PNW) Biochar Atlas (www.pnwbiochar.org) classified several biochars according to this classification, and production temperature and feedstock type of biochar have major influences on classification (Table 3). Other related classifications (e.g., fertility class) and assessments (e.g., cost-benefit analysis) can also be made by tools on IBI and PNW Biochar Atlas.

2.5. Half-life time

A half-life time is the time that elapses before half of biochar C mineralizes. It can be obtained by multiplying the MRT by the natural logarithm of 2 ($t_{1/2} = MRT * \ln 2$ or $t_{1/2} = \ln 2 / k$) (Lehmann and Joseph, 2015). Half-lives of the labile biochar C and the refractory C range dramatically from 2 to 462 days and 110 days to 76 years, respectively (Zimmerman et al., 2011). The broad range of soils ($n = 5$) and biochar types ($n = 19$, from 5 types of feedstocks at 250, 400, 525 and 650 °C) used in these experiments can be an explanation for the significant difference (Zimmerman et al., 2011). The logarithmic model proposed by Zimmerman (2010) can also be used to predict the half-life of biochar (Eq. 18).

$$C_{t_{1/2}} = \left(\frac{m+1}{2e^b}\right)^{(1/(m+1))} \quad (18)$$

Using the logarithmic model, Zimmerman (2010) obtained half-lives of biochar in the order of 10^2 to 10^7 years. Bai et al. (2013) compared the half-lives of biochar from pyrolysis of *Miscanthus* and hydrochar from hydrothermal carbonization of the same feedstock in different types of soils. The hydrochar has a half-life around a year or lower, while biochar ranges from 11 to 110 years depending on soil type and half-life calculation method (Bai et al., 2013). The half-life values of biochar vary dramatically. Although the half-life of biochar in sandy soil calculated by two-pool model (19.7 years) is much lower than that by the logarithmic model (110.7 years), the value in loamy soil by the former model (44.5 years) is much higher than that by the later model (18.7 years) (Bai et al., 2013). The half-lives calculated by the logarithmic model may be unreliable because the linear regression between logarithmically transformed experimental degradation rate (k) and incubation time (t) is very low ($R^2 < 0.4$) (Bai et al., 2013). However, the half-lives calculated by the one-pool and two-pool models seem comparable.

3. Limitations and recommendations

3.1. Incubation duration

Incubation duration may be the most influential factors to the calculation of biochar longevity (Chao et al., 2018). Mineralization rate of biochar in soil slows down gradually along with the incubation time. Longer incubation time leads to longer MRT due to the smaller mineralization rate used for modelling. Great difference can be observed when comparing half-lives (2–10 years) obtained from refs. (Bruun et al., 2012; Cross and Sohi, 2013), which were carried out with incubation duration of several days, to those (half-lives 27–193 years) of Zimmerman (2010) with a duration of one year. Modelled half-lives extended to 56–407 years when the incubation duration was lasted from

Table 2
Incubation experiment designing and data modelling details in case studies (ordered by incubation duration).

Ref.	Biochar type and C3/C4 origin	Incubation duration (year)	Application conditions and C3/C4 origin of soil	C mineralization determination	C mineralization data expression	Model	Biochar stability[a]
(Cross and Sohi, 2011)	Fresh, C4	0.04	Sand/soil, C3, incubation	$\delta^{13}CO_2$ flux	CO_2-C	NA[b]	NA
(Crombie et al., 2015)	Fresh	0.04	Sand/soil extract, incubation	CO_2 flux	% TOC[c]	NA	NA
(Awad et al., 2018)	Fresh	0.08	Soil, incubation	CO_2 flux	CO_2-C	NA	NA
(Lu et al., 2014)	Fresh, C4	0.08	Soil, C3, incubation	$\delta^{13}CO_2$ flux	CO_2-C	NA	NA
(Chaganti and Crohn, 2015)	Fresh	0.08	Soil, incubation	CO_2 flux	CO_2-C	NA	NA
(Lu et al., 2015)	Fresh, C4	0.08	Soil, C3, incubation	$\delta^{13}CO_2$ flux	CO_2-C	NA	NA
(Brassard et al., 2018)	Fresh	0.12	Soil, incubation	CO_2 flux	CO_2-C	NA	NA
(Hilscher et al., 2009)	Fresh	0.13	Soil, incubation	CO_2 flux	% TOC	NA	NA
(Rahman et al., 2018)	Fresh	0.15	Soil, incubation	$\delta^{13}CO_2$ flux	CO_2-C	NA	NA
(Tilston et al., 2016)	Fresh (^{14}C depleted)	0.15	Soil, incubation	$\delta^{13}CO_2$ flux + $^{14}CO_2$ flux	CO_2-C	NA	NA
(Hamer et al., 2004)	Fresh (biochar + ^{14}C labelled glucose)	0.16	Sand + microbial inoculant, incubation	$^{14}CO_2$ flux	CO_2-C	NA	NA
(Bamminger et al., 2014)	Fresh, C4	0.16	Soil, C3, incubation	CO_2 flux + soil δ^{13}C and biochar δ^{13}C	CO_2-C	NA	NA
(Bruun et al., 2012)	Fresh	0.18	Soil, incubation	CO_2 flux	CO_2-C	NA	NA
(Novak et al., 2010)	Fresh	0.18	Soil, incubation	CO_2 flux	CO_2-C	NA	NA
(Speratti et al., 2018)	Fresh	0.19	Soil, incubation	CO_2 flux + soil δ^{13}C and biochar δ^{13}C	CO_2-C/% TOC	NA	NA
(Farrell et al., 2013)	Fresh (^{13}C labelled)	0.2	Soil, incubation	$\delta^{13}CO_2$ flux	% TOC	NA	NA
(Sheng and Zhu, 2018)	Fresh	0.25	Soil, incubation	$\delta^{13}CO_2$ flux	CO_2-C	NA	NA
(Moreno-Barriga et al., 2017)	Fresh	0.25	Soil, incubation	CO_2 flux	CO_2-C	NA	NA
(Abbruzzini et al., 2017)	Fresh, C4	0.25	Soil, C3, incubation	$\delta^{13}CO_2$ flux	CO_2-C/% TOC	NA	NA
(Malghani et al., 2013)	Fresh, C4	0.29	Soil, C3, incubation	$\delta^{13}CO_2$ flux	CO_2-C/% TOC	NA	NA
(Calvelo Pereira et al., 2014)	Aged natural fire-derived char	0.3	Soil, incubation	CO_2 flux	CO_2-C	Double-exponential	MRT, 87–104 years
(Hansen et al., 2015)	Fresh	0.3	Soil, incubation	CO_2 flux	% TOC	NA	NA
(Bruun et al., 2008)	Fresh (^{14}C labelled)	0.31	Soil, incubation	$^{14}CO_2$ flux	% TOC	NA	NA
(Yin et al., 2014)	Fresh (^{13}C labelled)	0.31	Soil, incubation	$\delta^{13}CO_2$ flux	NA	NA	NA
(Keith et al., 2011)	Fresh (^{13}C depleted or C4)	0.33	Soil, incubation	$\delta^{13}CO_2$ flux	CO_2-C/% TOC	Double-exponential	MRT, 62–248 years
(Schulze et al., 2016)	Fresh	0.33	Soil, incubation	CO_2 flux	CO_2-C	One−/double-exponential	MRT, 4–15 years
(Murray et al., 2015)	Fresh	0.33	Soil, C4, incubation	$\delta^{13}CO_2$ flux	CO_2-C	Double-exponential	MRT, 22–1506 years
(Cheng et al., 2008)	Aged natural fire-derived char	0.48	Soil, incubation	CO_2 flux	CO_2-C	One-exponential	$t_{1/2}$, 59 years
(Luo et al., 2011)	Fresh, C4	0.49	Soil, C3, incubation	$\delta^{13}CO_2$ flux	CO_2-C	NA	NA
(Santos et al., 2012)	Fresh (^{13}C labelled)	0.49	Soil, incubation	$\delta^{13}CO_2$ flux	% TOC	Double-exponential	MRT,390–600
(Nguyen et al., 2014)	Fresh	0.52	Soil, incubation	$\delta^{13}CO_2$ flux	% TOC	Double-exponential	NA
(Bai et al., 2013)	Fresh	0.55	Soil, incubation	$\delta^{13}CO_2$ flux	% TOC	One-/double-exponential/power model	$t_{1/2}$, 19.7–44.5 years (double-exponential)
(Knicker et al., 2013)	Aged natural fire-derived char	0.6	Soil, incubation	CO_2 flux + soil δ^{13}C and biochar δ^{13}C	% TOC	Double-exponential	MRT, 11.7–40.6 years
(Naisse et al., 2015)	Fresh, C4	0.61	Soil, C3, incubation	$\delta^{13}CO_2$ flux	CO_2-C/% TOC	Double-exponential	$t_{1/2}$, 73.6 ± 5.6 years
(Ventura et al., 2015)	Fresh	0.67	Field	$\delta^{13}CO_2$ flux	CO_2-C/% TOC	NA	NA
(Singh et al., 2014)	Fresh (^{13}C labelled)	0.82	Field	$\delta^{13}CO_2$ flux	% TOC	NA	NA
(Zimmerman, 2010)	Fresh	1	Sand + microbial inoculant, incubation	CO_2 flux	CO_2-C	Power model	$t_{1/2}$, 100–100,000 years
(Fang et al., 2014a)	Fresh (^{13}C depleted)	1	Soil, incubation	$\delta^{13}CO_2$ flux	CO_2-C	Double-exponential	MRT, 214–610 years
(Maestrini et al., 2014)	Fresh (^{13}C labelled)	1	Field	$\delta^{13}CO_2$ flux	% TOC	One-exponential	Turnover time,191 years
(Budai et al., 2016)	Fresh, C4	1	Soil, incubation	$\delta^{13}CO_2$ flux	% TOC	Double-exponential	$t_{1/2}$, 4–252 years
(Wu et al., 2016)	Fresh (^{13}C labelled)	1.07	Soil, incubation	$\delta^{13}CO_2$ flux	% TOC	Double-exponential	MRT, 617–2829 years
(Bruun et al., 2014)	Fresh (^{14}C labelled)	1.13	Soil, incubation	$^{14}CO_2$ flux	% TOC	NA	NA
(Zimmerman et al., 2011)	Fresh, C4 or C3	1.37	Sand/soil, C3, incubation	$\delta^{13}CO_2$ flux	CO_2-C	Double-exponential	NA
(Herath et al., 2015)	Fresh, C4	1.4	Soil, C3, incubation	$\delta^{13}CO_2$ flux + soil δ^{13}C and biochar δ^{13}C	CO_2-C	NA	BC_{+100}, 20–~50%
(Liang et al., 2008)	Aged natural fire-derived char	1.5	Soil, incubation	CO_2 flux	CO_2-C	NA	Turnover time, several centuries to several millennia
(Hansen et al., 2016)	Fresh	1.83	Soil, incubation	CO_2 flux	CO_2-C/% TOC	NA	NA
(Stewart et al., 2013)	Fresh	1.92	Soil, incubation	$\delta^{13}CO_2$ flux	CO_2-C	NA	NA
(Rasse et al., 2017)	Fresh, C4	2	Soil, C3, field	$\delta^{13}CO_2$ flux	% TOC	NA	MRT, >100 years
(Kimetu and Lehmann, 2010)	Fresh, C4	2	Soil, C3, field	CO_2 flux + soil δ^{13}C and biochar δ^{13}C	CO_2-C	NA	NA

Table 2 (*continued*)

Ref.	Biochar type and C3/C4 origin	Incubation duration (year)	Application conditions and C3/C4 origin of soil	C mineralization determination	C mineralization data expression	Model	Biochar stability[a]
(Major et al., 2010)	Fresh, C3	2	Soil, C4, field	$\delta^{13}CO_2$ flux	CO_2-C	One-exponential	MRT, 600 years
(Fang et al., 2014b)	Fresh (^{13}C depleted)	2	Soil, incubation	$\delta^{13}CO_2$ flux	CO_2-C	Double-exponential	NA
(Fang et al., 2015)	Fresh (^{13}C depleted)	2	Soil, incubation	$\delta^{13}CO_2$ flux	CO_2-C	Double-exponential	MRT 25–1061 years
(Hilscher and Knicker, 2011)	Fresh (^{13}C labelled)	2.33	Soil, incubation	Soil $\delta^{13}C$ and biochar $\delta^{13}C$	% TOC	NA	NA
(Kuzyakov et al., 2009)	Fresh (^{14}C labelled)	3.2	Soil, incubation	$^{14}CO_2$ flux	% TOC	One-exponential	MRT, 200–2000 years
(Singh et al., 2012a)	Fresh, C4	5	Soil, C3, incubation	$\delta^{13}CO_2$ flux	% TOC	Double-exponential	MRT, 90–1600 years
(Kuzyakov et al., 2014)	Fresh (^{14}C labelled)	8.5	Soil, incubation	$^{14}CO_2$ flux	% TOC	One-exponential	MRT, 400–4000 years
(Weng et al., 2017)	Aged biochar (^{13}C labelled), C3	9.45	Soil, C4, field	$\delta^{13}CO_2$ flux + soil $\delta^{13}C$ and biochar $\delta^{13}C$	CO_2-C	NA	NA

[a] MRT: mean residence time. Only the MRT, $t_{1/2}$ or turnover time of the stable C pool is given.
[b] NA: not available.
[c] % TOC: percentage of the total organic carbon.

one year to 1173 days (3.2 years) (Zimmerman, 2010; Zimmerman and Gao, 2013). The mineralization rate of a 8.5-year incubation (Kuzyakov et al., 2014) is about 2.5 times lower than that reported based on data from the first 3.2 years (Kuzyakov et al., 2009). Although the mineralization rates stabilize gradually between the 4th and 5th year after incubation (Singh et al., 2012a), or between the 3rd and 8.5th incubation year (Kuzyakov et al., 2014), the rate keeps going down slightly. Nearly all residual biochar C consists of condensed aromatic moieties with labile C being degraded almost completely after 3.5-year incubation (Kuzyakov et al., 2014). Only about 6% of the initially added biochar was mineralized to CO_2 during the 8.5-years incubation (Kuzyakov et al., 2014). From the results obtained in refs. (Kuzyakov et al., 2014; Singh et al., 2012a, 2012b; Zimmerman and Gao, 2013), it seems that a minimum incubation duration of two years or preferably ≥3 years may be needed to obtain reliable biochar stability results.

The longest biochar decomposition study is about a decade with many studies being carried out within only one year (Table 2). Therefore, the available data in the references reflect mainly the decomposition of the relatively labile biochar C (Kuzyakov et al., 2014; Wang et al., 2016). It is possible that short-term incubation studies mainly monitor the mineralization of labile C components of biochar. Extrapolation of data from such studies may have considerably underestimated the MRT of biochar in soil. Evidence observed in the meta-analysis study also showed that longer duration led to lower decomposition rate and thus longer MRT (Fig. 2) (Wang et al., 2016). Based on the above discussion, the duration should be at least long enough to discriminate labile from recalcitrant C pools to facilitate the use of two-pool model. The MRT obtained from different studies may not be appropriate for comparison unless a similar duration was used.

Both the mineralizability of labile C pool and the pool size are important to decide the incubation duration (Wang et al., 2016). Labile C pool may be measured and exempted by labile C-reducing treatments such as H_2O_2- and heat-assisted oxidation (Edinburgh stability tool) (Cross and Sohi, 2013). If the degradation rates of pre-treated biochar and the recalcitrant C pool of untreated one is similar (needs verification in future studies), the incubation can be started from mineralization of recalcitrant C pool, thus reducing the experiment duration required. Many days even years of experiment time may be saved. Then biochar stability can be modelled by using the mineralization data of the recalcitrant C pool. However, close relationships between the labile C-reducing treatment degree and the mineralization rates (mainly for labile C) of biochar should be developed. It is quite a challenge to bridge such oxidative stability with the biotic & abiotic stability of biochar in soil. Some researchers have tried to do so. The MRT of the H_2O_2- and heat-assisted oxidized charcoal (1.7%) was assumed to be 45 years (Cross and Sohi, 2013). It is based on the assumption that the manmade biochar was similar to the natural wildfire charcoal, and the oxidation of biochar is equivalent to charcoal mineralization in soil (Cross and Sohi, 2013). More studies can be done to investigate the incubation of labile C-removed biochar which has only a recalcitrant C pool.

3.2. Biochar mineralization determination

3.2.1. Biochar mineralization determination by CO_2 efflux

The CO_2 release after biochar application in soil may result from the biodegradation of biochar components, abiotic release from carbonates or chemi-sorbed CO_2 and priming of native soil organic carbon (SOC) pools (Ameloot et al., 2013). Efflux CO_2, rather than biochar C remained in soil, is used as a surrogate for documenting the degradation of biochar C in most published studies since direct sampling of biochar in soil is much more difficult (Table 2). However, many studies used the simple evaluation of total CO_2 efflux without a separated assessment of CO_2 sources (Table 2). The mineralization of biochar C is thus not separated from the mineralization of soil components (e.g., SOC), ignoring the priming effect of biochar on SOC (Kimetu and Lehmann, 2010; O'Toole et al., 2013). This approach may lead to large deviation to the mineralization rate depending on the priming effect. This differentiation problem may be avoided by incubating biochar in aerobic and carbon-free sand (Nguyen et al., 2010; Zimmerman, 2010). However, incubation of biochar under such conditions overlooks the effect of interactions between real soil component and biochar on biochar stability (Smith et al., 2010).

3.2.2. Biochar mineralization determination by C isotopic signatures

Employing biochars with ^{13}C isotopic signatures ($\delta^{13}C$, Eq. 19) different from the SOC allows differentiating biochar derived CO_2 efflux from that of SOC if the $\delta^{13}C$ signatures of the two materials are identical (Singh et al., 2012a).

$$\delta^{13}C = \left(\frac{\left(\frac{^{13}C}{^{12}C}\right)_{sample}}{\left(\frac{^{13}C}{^{12}C}\right)_{standard}} - 1 \right) \times 1000‰ \quad (19)$$

$^{13}C/^{12}C$ ratio is the basis for classifying C3 and C4 plants because of their different pathways for photosynthetic carbon dioxide fixation (Bender, 1971). Incubating biochars derived from C4 feedstocks in soil dominated by C3 organic matter is the common way to achieve the source differentiation of the mineralized CO_2 during incubation (Malghani et al., 2013; Purakayastha et al., 2016; Singh et al., 2012a). The $^{13}C/^{12}C$ ratio difference between mineralized CO_2 (calculated or analyzed directly) and biochar C/SOC can be used to calculate the fraction of CO_2 evolved from biochar. This produces an accurate biochar C mineralization rate. However, the natural abundance method based on

C3/C4 has its limitations; if $\delta^{13}C$ of biochar or $\delta^{13}CO_2$ evolved from biochar are within the same range as those of soil, which means the ^{13}C natural abundance of biochar C and SOC is similar, then the isotopic technology would be much less effective to differentiate CO_2 sources (Zimmerman et al., 2011). In some other situations, $\delta^{13}C$ may become insufficiently sensitive for reliable deployment because biochar-derived C makes a much smaller contribution to the CO_2 flux in comparison with SOC and vice versa. In addition, frequent or continuous measurements require considerable effort and expenses input.

Artificially C-labelled biochar can be more efficient to obtain identifiable C signatures and it can be obtained by ^{13}C and ^{14}C labelling of biochar or depletion of ^{13}C from biochar. These techniques have been used by many researchers to quantify the biochar mineralization rate (Dai et al., 2017; Fang et al., 2014a; Kuzyakov et al., 2014; Wu et al., 2015). One of the reported longest laboratory incubation study (8.5 years) used ^{14}C-labelled biochar to trace C mineralization to CO_2 (Kuzyakov et al., 2014). The labelling of ^{13}C or ^{14}C is normally done by pulse-labelling method (Yin et al., 2014) or by growing plant under ^{13}C or ^{14}C enriched atmosphere in a closed environment (Bruun et al., 2014). Alternatively, the depletion of ^{13}C from biochar, e.g., by growing plant under ^{13}C depleted atmosphere can be used to label biochar without ^{13}C, achieving the differentiation from the SOC (which is marked with ^{13}C) (Fang et al., 2014a, 2014b, 2015). However, it is not known if there are preferential locations for carbon-labelling in the charred material that is only partially labelled. For example, only char from roots of barley was homogeneously labelled by ^{14}C with acceptable activity, but not for char from other part of the plant (Bruun et al., 2008). Therefore, homogenous biomass labelling is very difficult and is also extremely expensive.

3.2.3. Biochar mineralization determination by biochar residue in soil

The mineralized biochar C calculated from the variations of biochar C stocks remained in soil can be used for modelling. The biochar ^{13}C resided in soil can be determined by ^{13}C NMR technology, and the mineralization of biochar C can be calculated by difference (Hilscher et al., 2009). However, this approach is based on a known C input and quantifiable physical biochar mass losses such as erosion, translocation, leaching/solubilization, volatilization and consumption by later fires, which are not easy to be achieved especially in field studies. The high heterogeneity of biochar distribution in a field experiment leads to large variability over time although with only a small difference in stock. Even repeated measurements of soil ^{13}C derived from the biochar application would give an erroneous and low estimation of MRT if a significant physical biochar mass loss occurs (Major et al., 2010). For example, erosion of biochar can lead to an ~150-year difference error in turnover time depending on the extent of erosion occurred (Abney and Berhe, 2018).

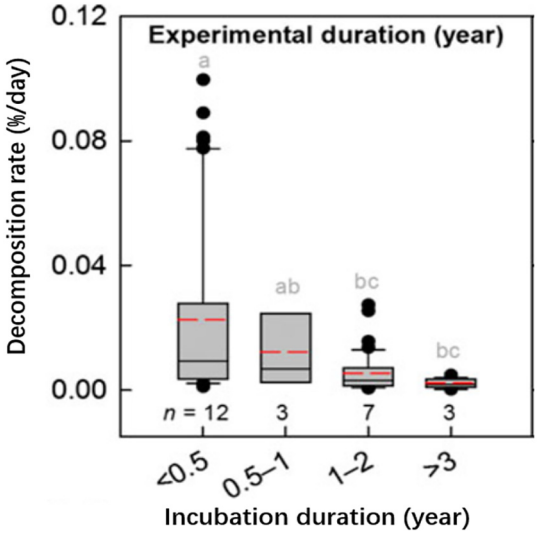

Fig. 2. Comparisons of biochar decomposition rates from studies with different incubation duration. The black solid and red dashed lines, lower and upper edges, bars and black circles represent the median and mean values, 25th and 75th, 10th and 90th percentiles, and outliers of all data, respectively. Number of studies included from each group is inserted next to x-axis (Wang et al., 2016).

Table 3
Carbon class of biochar from Pacific Northwest (PNW) Biochar Atlas (www.pnwbiochar.org) [a]

Production parameter	Pyrolysis 300 °C	Pyrolysis 500 °C	Pyrolysis 700 °C
Softwood (Douglas fir)	2	5	5
Hardwood (Oregon White Oak)	2	5	5
Nuts (Hazelnut shells)	2	5	5
Manure (Poultry Litter Pellets)	1	2	2
Yard Debris	2	3	5
Spent Grain (Spent Brewers Grain)	1	4	5

[a] The number in the table represents the carbon class: class 1 with $sBC_{+100} < 300$ g kg^{-1}; class 2 with 300 g kg^{-1} ≤ sBC_{+100} < 400 g kg^{-1}; class 3 with 400 g kg^{-1} ≤ sBC_{+100} < 500 g kg^{-1}; class 4 with 500 g kg^{-1} ≤ sBC_{+100} < 600 g kg^{-1}; class 5 with sBC_{+100} ≥ 600 g kg^{-1}.

3.3. Laboratory and field study

Besides the issues stem from the mineralization modelling, the factors influencing the variation of modelling results include biochar application environment such as soil type, temperature, moisture, microbial community, clay mineralogy and soil texture during field studies. Most current assessment results of biochar stability come from short-term laboratory incubations, due to the advantages of time-saving, small sample demand, controllable conditions and ease for more comparison studies, etc. Control over experimental conditions allows the investigation of the effects of different environments and biochar properties on biochar mineralization and allows more reasonable explanation for the large variations of calculated MRT between and within studies. Another important advantage may be the opportunity to utilize the so-called aged biochars obtained from historic charcoal (Cheng et al., 2008) or experimentally produced in the laboratory by oxidants (Cross and Sohi, 2013). However, laboratory incubations are commonly carried out in a closed laboratory chamber. They can never truly simulate field conditions. For example, the possible decrease in microbial biomass over laboratory incubation time particularly in long-term laboratory incubations may also cause biochar mineralization variation (Kimetu and Lehmann, 2010; Zimmerman and Gao, 2013). Reduced degradation rate may be obtained and used for biochar stability assessment, resulting in underestimation. These major shortcomings cannot be overcome simply by developing appropriate degradation models.

Field study, on the other hand, provides unique and essential data for obtaining the estimation of biochar stability under varied real-world conditions such as soil type, soil management (e.g., tillage), differential climate, constant organic C input, and presence of plants (e.g., root). Due to the large variation of these factors, the estimated MRT of biochar spanned three orders of magnitude, from years to millennia with great uncertainty (Gurwick et al., 2013). The orders of the magnitude of MRT from 6 to 5448 years (adjusted to 10 °C) was obtained from field studies as reviewed in ref. (Lehmann and Joseph, 2015). The uncertainties may also come from C loss by other pathways such as biochar disappearance from the topsoil, erosion, leaching or burning (Abney and Berhe, 2018). The significant unknown export would underestimate or even erroneously estimate the persistence of biochar. The use of C isotope can be used in filed studies to estimate CO_2 efflux and possible lost by downward migration (by using soil isotopic mass balance) to improve the assessment (Ventura et al., 2018). Additionally, field studies restrict the number of comparisons between biochar types. Field chronosequence substitutes space for time by sampling soils that

Table 4
Strategies to increase the accuracy of the incubation and modelling biochar assessment methods.

Procedure		Strategies	Comments
Experiment designing	Incubation duration	■ Duration depends on labile C pool size and mineralizability; 2–3 years or longer is recommendable without available data on labile C. ■ Use of labile C-reducing treatment to eliminate the duration of labile C mineralization.	■ Without labile C-reducing process, data from short-term incubation duration is not suitable for calculating biochar stability; ■ Correlate oxidative stability with biotic stability of biochar is not easy to achieve.
	Biochar mineralization determination	■ Use the difference on ^{13}C natural abundance between biochar C (C4) and SOC (C3) to detect $\delta^{13}CO_2$ flux; ■ Use ^{13}C- or ^{14}C-labelling technology by pulse-labelling method or by growing plant under ^{13}C or ^{14}C enriched/depleted atmosphere to detect $\delta^{13}CO_2$ or $^{14}CO_2$ flux; ■ Analyze biochar C content directly by BPCAs and ^{13}C NMR, etc.	■ Use general CO_2 flux will not be able to differentiate the CO_2 releasing source (either from biochar or soil); ■ The direct biochar C content analysis is less feasible especially in the field due to biochar lose in other ways; ■ C isotopic technology is very expensive; ■ The mineralization rate difference between biochar C and soil C has a big influence on applicability of using ^{13}C natural abundance difference and even of using ^{13}C-labelling.
	Laboratory or field study	■ Field study is preferable to laboratory study; ■ Laboratory study may be designed to simulate field study with more variables; ■ Chronosequence char can be used to assess very long-term performance.	■ Field study is too complex with many variables; ■ Chronosequence of fire-cleared soil (with char) has no input data; Chronosequence of fire-cleared soil from different place has varied environmental conditions.
Modelling	Model selection	■ Multiple C pools may be better, but the degree of fitting should be good; ■ At least double-exponential model should be used; ■ Elimination of the mineralization data of labile C before modelling may improve the assessment.	■ Modelled results are suggested to compare with the data from meta-analysis study; ■ Multiple C pools may have risk of over-fitting; ■ More powerful and robust dynamic models may be developed.
	Data expressions and data constraints	■ Data constraints are preferred, unconstrained fitting should be avoided; ■ % TOC mineralized is preferred to CO_2 flux in mass or flux in %.	■ There is potential problem in overestimating the pool sizes by unconstrained fitting; ■ For the fitting on flux data, the kinetic parameters are only representative for the C-stock contributing to the flux, whereas for the % TOC mineralized approach the turnover refers to the entire carbon stock in the soil.
Characterization of biochar and the application environment		■ Characterization of microbial available C, elemental analyses (C, H, N, and O), surface area, pore size distribution, pH, and volatile matter/ash content as well as production conditions (e.g., pyrolysis temperature and residence time) and feedstock type; ■ Record soil type, SOC, soil clay content, temperature, pH, moisture, and soil microorganisms and fauna. ■ Use of standard (reference) biochar materials	■ Promote the correlation between biochar stability and biochar properties (e.g., H/C_{org} and O/C_{org}); ■ Facilitate future biochar stability studies by providing variables for results adjustment, e.g., temperature adjustment or by providing referential results obtained from using standard (reference) biochar materials.

received biochar-type C at chronosequential times in the past. Therefore, field chronosequence allows for a theoretical examination of biochar mineralization over longer periods of time up to hundreds to even thousands of years (Cheng et al., 2008; Liang et al., 2008; Nguyen et al., 2009). However, this approach requires a sufficiently large number of sites that received the same amount and type of biochar C, under similar environmental conditions and management. It has the same constraints as the common field study.

The field study is so complex that the factors which are found to be substantial to biochar mineralization under some environmental conditions may be negligible in other cases. In research carried out by Rasse et al. (2017), biochar showed high stability in both laboratory incubation and field trial during the 90-day study. It is vital important to carry out more studies by comparing long-term laboratory degradation data to those of field studies of different types.

3.4. Modelling and calculation

3.4.1. Selection of models

Most studies used the two-pool model, and the comparison results between two-pool model and one-pool model shows that MRT/half-life time modelled from two-pool model is longer than the one-pool one (Bai et al., 2013). For example, by using data from ref. (Singh et al., 2012a), MRT values of 966, 1614 and 16,313,528 years were obtained from modelling by one-pool, 2-pool, and power model equations, respectively (Lehmann and Joseph, 2015). Zimmerman and Gao (2013) compared the results obtained from one-pool, two-pool and power modelling of C mineralization of grass and oak biochars in abiotic incubation or microbial incubation (Fig. 3). The half-lives evaluated by two-pool model were found generally higher than those by one-pool model, while the half-life of grass biochar produced at 650 °C is about ten-fold higher (3225 vs. 358 years) in abiotic incubation, and is more than five-hundred-fold higher (74,921 vs. 133 years) in microbial incubation (Fig. 3). Moreover, the half-life obtained by power model is increased dramatically to at least in centennial to hundreds of millions of years (Fig. 3). Whereas, that of grass biochar produced at 650 °C modelled by power model unexpectedly decreased to 2700 years (not fitted well, $R^2 = 0.66$), which is only 1/10 of that of grass biochar produced at 250 °C (Fig. 3). More unexpectedly, grass biochar, in many cases, was found with much higher half-lives than those of oak biochar which should be more stable than grass biochar (Fig. 3). The data obtained by power model may not be reliable because of low fitting degree. The data fit the best with two-pool model ($R^2 > 0.97$) and the least with power model ($R^2 = 0.66$–0.97) (Fig. 3). This phenomenon was also observed by Bai et al. (2013).

In order to adequately describe the mineralization dynamics, two-pool model should be indispensably used at least. The applicability of models may depend largely on the availability of data collected and the mineralizability of different C pools of biochar. Using a higher number of C pools in the model may require longer-term observations and more measurements for parameterization of models. The difference between one- and two-pool models would be relatively evident for the biochars with lower BC_{+100} value or higher mineralization rate/high labile C content (Lehmann and Joseph, 2015).

Alternatively, it may be possible to fit curves by omitting the initial rapid mineralization data. By doing this, the mineralization of labile C pool can be neglected and the estimated MRT/half-life or percentage of biochar remained in soil could be much higher than that without omission. This omitting procedure can be used as effective as the labile C-reducing treatments. In this case, one-pool model may be used.

3.4.2. Fitting procedures

According to the difference of data expressions (CO_2 flux and percentage of total organic carbon mineralized, that is % TOC mineralized)

and data constraints (constrained and unconstrained), there are four different fitting approaches during data modelling (Weihermüller et al., 2018): i) constrained fitting on CO_2 flux data using pool sizes expressed on mass basis (e.g., mg CO_2/g soil), where C_1 to C_n sum up to total cumulative flux at t_{end}; ii) constrained fitting on flux data using pool sizes expressed in % from total flux, where C_1 to C_n sum up to 100% total cumulative flux at t_{end}; iii) unconstrained fitting on flux data using pool sizes expressed on mass basis (e.g., mg CO_2/g soil), where C_1 to C_n will sum up to any value; iv) constrained fitting on % TOC mineralized data using pool sizes expressed in % from total TOC mineralized, where C_1 to C_n sum up to the total % TOC mineralized at t_{end}. The use of different fitting procedures leads to varied results in the pool sizes and kinetic parameters (Weihermüller et al., 2018).

Mineralization data from Mukherjee (2015) were fitted to these four approaches by double-exponential model (Fig. 4) and obtained with labile C pool of MRT ranging from 13.1 to 16.2 years, and recalcitrant C pool of MRT ranging from 362 to 2273 years. Unconstrained fitting is likely to be unreliable because the sum of each estimated pool size will not necessarily match the total C-stock in the microcosm (Weihermüller et al., 2018). In approaches i) and ii), only the mineralized C-pools will be analyzed, without analyzing the kinetics of the entire C-stock; the fitted rate constants (k_n) will generally be higher, and the MRTs and half-lives will be much shorter than those obtained by approach iv) (Weihermüller et al., 2018). Constrained data expressed as % TOC mineralized (approach iv)) would be more appropriate for modelling. These four approaches have been used by different researchers (Table 2) and therefore, considerable variation on MRT (C pool size or mineralization rate) between studies may be partly due to the varied fitting approaches. In addition, over-fitting and ill-posed fitting (non-uniqueness, with multiple parameter combinations that can explain the measured data equally good) when using models with higher number of C pools may also result in unrealistic C-pool sizes and rate constants (Weihermüller et al., 2018). The application of proper statistical metrics for the judgment of over-fitting is suggested to overcome the over-fitting problems. The ill-posed fitting is inherent to the experimental data and the nature of the simple carbon decay model given and is likely to be unavoidable. Complex predictive carbon models such as RothC, Century, Candy, and Yasso may be developed for modelling in addition to the simple exponential carbon decay model.

3.4.3. Meta-analysis

Meta-analysis of biochar stability from multi-case data pool can be more indicative than individual cases. The biochar stability from individual studies may first be compared with the meta-analysis results to get a general evaluation of the accuracy of the obtained results. There are several meta-analysis studies. Results from the first meta-analysis of 16 studies with double-exponential model ($R^2 = 0.44$, $n = 54$, root mean square error = 8.35) indicate that the labile C pool (17%) has MRT of 3 years, while the recalcitrant C pool (83%) has an average MRT of 870 years (Singh et al., 2012b). Gurwick et al. (2013) reviewed the studies related to biochar stability, transport or fate under field conditions; only seven of these studies estimated biochar decomposition rates in situ and calculated MRTs of 8–4000 years. Another recent meta-analysis which used data from 24 studies using stable (^{13}C) and radioactive (^{14}C) carbon isotopes to estimate the MRT of biochars by double-exponential model ($R^2 = 0.16$, $n = 128$), however, obtained MRTs of labile C pool with 108 ± 196 days and recalcitrant biochar C pool with 556 ± 483 years, with pool sizes of 3 ± 0.6% and 97 ± 0.6%, respectively (Wang et al., 2016). Although the mean values are indicative, the meta-analyzed data are quite scattered, and large difference between these two meta-analysis studies were observed. Considering the second meta-analysis study used only data from observing ^{13}C and ^{14}C carbon isotopes, it should be more reliable.

3.5. Characterization of biochar and use of standard (reference) biochar

Apart from strategies discussed above and listed in Table 4, characterization of biochar and use of standardized (reference) biochar during incubation could significantly promote biochar stability assessment.

3.5.1. Characterization of biochar

Due to the time-consuming and costly disadvantages of incubation study, biochar properties obtained from analysis of ultimate, proximate, aromaticity, degree of aromatic condensation and chemical degradation resistance would eventually be used as proxies for biochar stability assessment (Cross and Sohi, 2013; Harvey et al., 2012; Kaal and Rumpel, 2009; Leng et al., 2018; McBeath et al., 2011; Spokas, 2010; Wiedemeier et al., 2015). H/C_{org} and/or O/C_{org} are being developed as promising proxies for biochar stability evaluation (see Section 2.4). Although the correlations between biochar mineralization and some of the proxies such as H/C_{org} are very identical in some individual studies, those for global data set remain weak due to the large variations of biochar properties (e.g., feedstocks and pyrolysis conditions), soil environment (e.g., soil type, SOC content, temperature, and moisture) and other factors such as vegetation (presence of plant roots) and tillage between studies. For example, the presence of plant roots resulted in much higher biochar degradation rates and reduced MRT than that in the absence (Ventura et al., 2018). Characterization of biochar is pivotal to correlate biochar persistence/stability with biochar properties that can be evaluated readily after biochar production. Biochar stability studies are suggested to include characterization of a minimum set of properties of the specific biochar and the environment it is applied to. Biochar properties should include microbial available C, elemental analyses (C, H, N, and O), surface area, pore size distribution, pH, and volatile matter/ash content as well as production conditions (e.g., pyrolysis temperature and residence time) and feedstock type. Environment record may include soil type, SOC, soil clay content, temperature, pH, moisture, and soil microorganisms and fauna. These parameters can play great roles in the stability of biochar in soil. The content of nitrogen in biochar and soil should also be included when emissions of nitrogen oxides such as N_2O constitutes a considerable release from the matrix. N_2O has been identified as strong GHG, and N_2O flux was found positively correlated with biochar in soil in some studies (Brassard et al., 2016).

On the other hand, simultaneous characterization of biochar and the application environment are useful strategies to the development of future biochar stability studies. Adjustment of biochar stability results by correction of variables is needed when comparing results from different sources. The temperature conversion index Q_{10} (temperature sensitivity of biochar) can describe the relationship between mineralization of biochar and the application temperature, which has been used as an ideal indicator for adjustment of biochar stability results obtained from various sources (with different temperatures). It is defined as the increase rate in mineralization with a temperature increase of 10 °C and the Q_{10} values decrease non-linearly with increasing mineralization temperature [$Q_{10} = 1.1 + 12.0 * \exp(-0.19 * T)$] (Lehmann and Joseph, 2015). The correction of other factors such as SOC may be a next step for such adjustment due to the great role of the priming effect on biochar C mineralization. It could be very challenging because of different response of the reaction rate of SOC degradation to temperature and the complex interactions between SOC and biochar (Fang et al., 2014b; Karhu et al., 2010).

3.5.2. Use of standard (reference) biochar

Use of standard (reference) biochar can also promote the development of biochar stability assessment. Biochar standardization and legislation harmonization are making the progress for standardizing biochar production procedures (Meyer et al., 2017). By using a standard procedure, the biochars used in different studies but produced from the same feedstock and production procedures can bear similar characteristics, facilitating the comparison between studies.

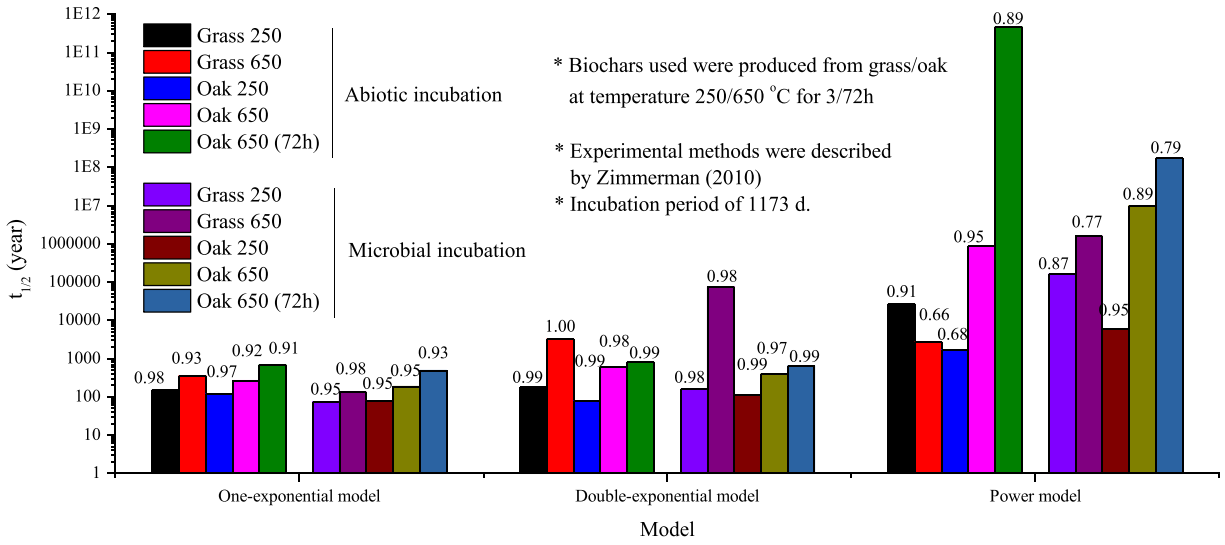

Fig. 3. Comparison of laboratory incubation biochar degradation rate parameters using three different degradation models (Zimmerman and Gao, 2013). Numbers above the bar represent the correlation coefficient for the fitness of the model to the data; for double-exponential model, only the $t_{1/2}$ of the recalcitrant biochar C pool was shown.

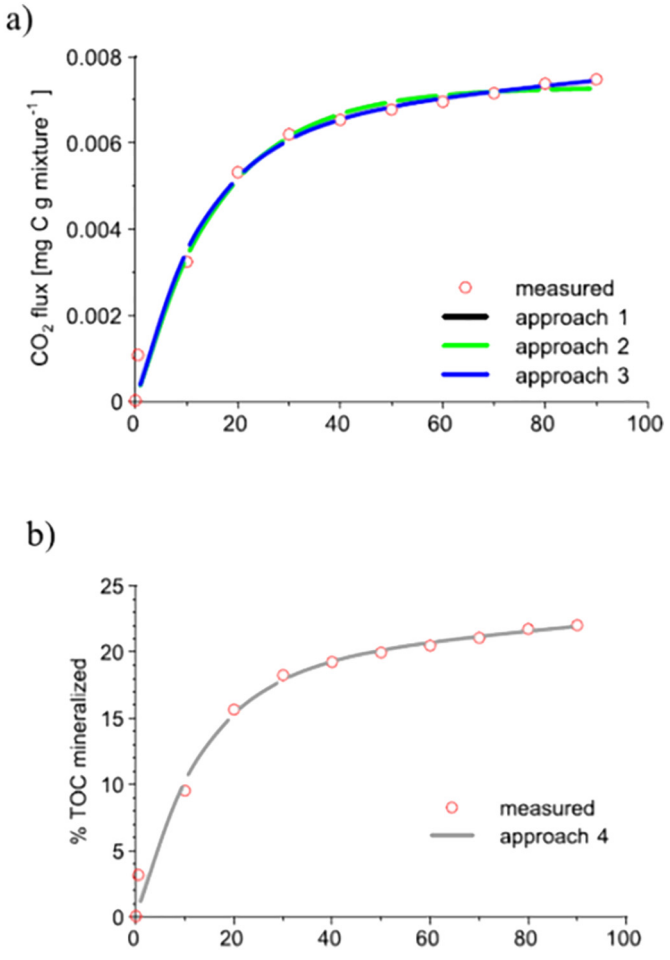

Fig. 4. Fitted results of the four different model approaches (approach 1=Constrained fitting on flux data using pool sizes expressed on mass basis, approach 2=Constrained fitting on flux data using pool sizes expressed in % from total flux, approach 3=Unconstrained fitting on flux data using pool sizes expressed on mass basis, and approach 4=Constrained fitting on % TOC mineralized data using pool sizes expressed in % from total TOC mineralized) (Weihermüller et al., 2018).

Excitingly, organizations such as the UK Biochar Research Centre (UKBRC) at the University of Edinburgh are already providing standard biochar materials for researchers to use as samples or references. A set of 12 standard biochar materials (Edinburgh Standard Biochar set) had been released freely to the global research community since 2015 and they have been supplied to over 80 research groups on five continents (Mašek et al., 2018a, 2018b). The use of such standardized reference materials simplifies the comparison of different studies and facilitates the replication of researches or benchmarks findings of other researchers (Mašek et al., 2018b; Sedlak, 2018).

4. Concluding remarks

Biochar stability is decisive to its utilization for carbon storage. Incubation experimental designing and modelling methods, e.g., incubation duration, models and fitting methods, incubation environment (laboratory or field) and biochar C mineralization determination and mineralization data expression forms (as flux or % TOC mineralized), introduce considerable variations to the assessment results of biochar stability. Longer incubation duration, modelling incubation data with double-exponential model, using C isotopic technology for CO_2 evolution determination and express as % TOC mineralized with biochar applied in the field are favorable to obtain biochar stability of high accuracy.

Strategies such as biochar labile C-reducing treatment (e.g., oxidation), omission of the initial rapid biochar C mineralization phase, utilization of field chronosequence chars, taking advantages of available meta-analysis results, adjustment of the biochar stability results by correction of variables (e.g., Q_{10} for correction of temperature), the use of standard (reference) biochar materials, and simultaneous characterization of biochar and the application environment are possible ways to further improve biochar stability assessment methods or contribute to the development of future biochar stability studies.

More importantly, the standardization of biochar stability assessment methods is needed. Current experimental studies on biochar stability assessment may follow the strategies proposed in this review to avoid improper use of experiment designing and data modelling methods.

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